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ACID RAIN AUDITS
-1988-

by

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SECTION 1

INTRODUCTION

The National Performance Audit Program (NPAP) is conducted by the Atmospheric Research and Exposure Assessment Laboratory (AREAL) of the U.S Environmental Protection Agency (EPA) at Research Triangle Park, NC. NPAP provides EPA management a means to assess the analytical proficiency of state and local laboratories. The acid rain audits, which are a part of the NPAP program, are open to governmental, academic and commercial organizations. Participation is voluntary.

When our acid rain audit program began in 1975 it was restricted to members of the World Meteorological Organization (WMO). In 1981, U.S. participants of the NPAP who were known to be routinely analyzing acid rain samples were invited to participate in an acid rain audit conducted only for U.S. laboratories. Thirty-two laboratories accepted the invitation and 18 actually reported their results.

In 1988, participation in the U.S. acid rain audit program was opened to all NPAP participants. One hundred and fourteen agencies accepted the invitation for the May 1988 (0588) audit and 118 accepted the invitation for the October 1988 (1088) audit. However, only 57 of these laboratories (50%) returned results for the 0588 audit and only 51 (43%) returned results for the 1088 audit. We believe these low levels of participation in the 1988 audits resulted because many agencies that requested to participate were unfamiliar with the extensive analyses required for precipitation samples. When they received the samples they decided not to analyze them. Only 52% of the results reported came from laboratories who had been regular participants in the previous audits.

SECTION 2

PROCEDURE

The five samples used in the audit are contained in polyethylene containers to improve sample stability. The participating laboratories analyze three of the samples for pH, conductivity, acidity and the cations and anions normally measured in precipitation samples. The other two samples, which are acid stabilized to prevent loss of metals from the solution, are analyzed for heavy metals.

The samples are prepared using formulations developed by the National Institute of Standards and Technology (NIST) and certified by an independent analytical (referee) laboratory using NIST reference materials. The participants analyze the samples using the analytical procedures they normally employ when analyzing their precipitation samples. Each laboratory is shipped a set of samples consisting of one sample from each of the five series. When diluted 1:50, each sample simulates a precipitation sample.

The participants dilute each sample, analyze it in triplicate and average the results for each analyte. They also analyze at least one blank of the distilled water they used to dilute the samples to correct their results for any contribution from the distilled water. All results are then forwarded to EPA for summarization and evaluation. Each participant is then sent a report that compares his results to the expected values for each analyte. At the end of the year, this summary report is prepared so that all participants can see how their performance compared to that of the other laboratories.

SECTION 3

RESULTS AND DISCUSSION

The data and statistics in this report are descriptive of the quality of the analytical data currently being reported by agencies measuring acid rain. At present, there are no federal regulations specifying the accuracy required in the analysis of acid rain samples. Therefore, we recommend that individual laboratories evaluate their progress and improve their analytical capabilities as they feel necessary based on their own results and the averages reported in this report for the 0588 and 1088 acid rain audits.

Less than 35% of the 1988 audit participants analyzed all samples for all the analytes. The approximate percentage of participants who reported results for each analyte or class of analyte (minor ions, heavy metals) are pH and conductivity, 94%; acidity, 26%; sulfate and nitrate, 69%; minor anions (F, Cl), 31%; minor cations (NH_4, Ca, Mg, Na, K), 46%; and heavy metals (Mn, Fe, Cd, Cu, Ni, Pb, Zn), 33%. These percentages are generally lower than those for the previous audits.

The number of audit participants is small and less than 50% of the participants analyze for the minor anions (Cl, F), cations (NH_4, Ca, Mg, Na, K) and heavy metals (Mn, Fe, Cd, Cu, Ni, Pb, Zn). Further, the concentrations of many of the analytes are near or below the quantification limits of the analytical methods, so many participants report their results to only one significant figure (despite our request to report them to two significant figures). For the above reasons, it is difficult to obtain a sufficient number of results on which to perform an in-depth statistical analysis. For example, suppose a laboratory obtains a value of 0.14 mg per L for Na when the true value is 0.15 mg per L but only reports a value of 0.1 mg per L. The apparent error is -33% but in actuality it is only -7%.

Also, in previous audits, we had observed that many participants had relatively large positive and negative percent differences for analytes in the same general class (anions, cations, metals) even though the same analytical method was used to determine all the analytes in that class. It was also observed that participants who had participated in many of the previous audits tended to show large variations in the magnitude and size of the percent difference for the same analyte from one audit to the next. This variation was quite randomly distributed.

To remove as much of these random variations as possible from the data, it was decided to calculate a percent difference by level for each laboratory for each class of analyte rather than calculate a percent difference for each analyte within each class of analyte (the approach used in earlier reports). This was accomplished by determining the sum of the concentrations for all the analytes in a specific class for the expected and for the reported values. The difference between the two sums was then determined and the percent difference --(reported-expected) 100/expected--was calculated.

In the case of the minor anions and the minor cations almost all participants who reported results for one analyte in these classes reported results for all the analytes in these classes. Thus, the percent difference for each participant for each analyte class was used to calculate the average percent difference for that analyte class, i.e., cation, anion.

However, because a significant number of the participants who reported results for the metals did not analyze for all seven of the metals, it was decided to report each participant's average percent difference and not to combine them to obtain a grand average.

Tables 1 and 3 present the results reported (n) for all analytes except the heavy metals for the 0588 and 1088 audits, respectively. Tables 2 and 4 present the results for these two audits after outliers were removed using an outlier rejection method that is based on the standard deviation historically obtained for these audits. This procedure considers all percent differences that exceed 3 times the historical standard deviation (10% for these audits) to be outliers (1). For information purposes, the concentrations of the individual anions and cations in the 1988 samples are presented in Table 5.

Tables 6 through 9 present the results for the 0588 and 1088 audit samples that contained the heavy metals. Tables 6 and 8 present the results reported by all participants for the 0588 and 1088 audits, respectively. Tables 7 and 9 present the results after outliers were removed. For information purposes, the concentrations of the individual metals in each 0588 and 1088 audit sample is presented in Table 10.

A comparison of Tables 1 and 2 and a comparison of Tables 3 and 4 demonstrate that quite a few participants encountered difficulty measuring acidity and the cations and anions. The number of outliers reported is larger than those reported for 1985, 1986 and 1987. It is quite possible that this increase resulted because many laboratories were analyzing this type of synthetic precipitation sample for the first time. Also, the lower the concentration of the analyte, the higher percentage of the results that were rejected as outliers. This is consistent with the previous audits. Unfortunately, a majority of precipitation samples contain ions at these levels.

Inspection of the average results for 1985, 1986 and 1987 (2,3,4) and those in this report for the analytes most frequently measured show no trend in the performance obtained from audit to audit.

Inspection of the individual laboratory results for the heavy metals (Tables 6, 7, 8 and 9) shows that most laboratories obtained results that agreed very well with the expected value in both 1988 audits. When a laboratory reported results that differed markedly from the expected value in one audit, it generally showed good agreement between the expected and reported values in the other 1988 audit.

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Table 1. Results Reported For All Analytes Except Heavy Metals--0588 Audit

Audit	Analyte	Sample	N	Average Reported Value	Expected Value	% Diff.
0588	pH	1	52	4.37	4.40	-0.68
		2	52	3.53	3.50	0.86
		3	52	3.55	3.52	0.85
	Conductivity	1	48	20.98	16.50	27.15
	µS/cm	2	48	148.00	156.00	-5.13
		3	48	133.00	130.00	2.30
	Acidity	1	17	56.82	41.10	38.24
	µeq/L	2	17	262.00	312.00	-16.02
		3	17	268.00	292.00	-8.22
	SO_4	1	38	0.80	0.66	21.21
	mg S/L	2	40	4.48	3.91	14.58
		3	40	3.37	2.89	16.61
	NO_3	1	38	0.38	0.11	245.45
	mg N/L	2	40	2.24	2.14	4.67
		3	40	1.89	1.81	4.42
	Anions (Cl, F)	1	19	0.43	0.33	30.30
	mg/L	2	21	3.03	3.21	-5.61
		3	20	1.45	1.42	2.11
	Cations	1	22	0.50	0.42	19.05
	(NH_4, Na, Ca,	2	25	4.00	3.86	3.63
	Mg, K)	3	22	1.15	1.02	12.75
	mg/L					

Table 2. Table 1 Results After Outliers Removed

Audit	Analyte	Sample	N	Average Reported Value	Expected Value	% Diff.
0588	pH	1	51	4.40	4.40	0.00
		2	52	3.53	3.50	0.86
		3	52	3.55	3.52	0.85
	Conductivity	1	42	18.44	16.50	11.76
	µS/cm	2	43	147.00	156.00	-5.76
		3	46	127.00	130.00	-2.31
	Acidity	1	5	40.14	41.10	-2.34
	µeq/L	2	12	342.00	312.00	9.62
		3	11	319.00	292.00	9.25
	SO_4	1	31	0.66	0.66	0.00
	mg S/L	2	36	4.02	3.91	2.81
		3	35	2.96	2.89	2.42
	NO_3	1	34	0.11	0.11	0.00
	mg N/L	2	38	2.13	2.14	-0.47
		3	38	1.81	1.81	0.00
	Anions (Cl, F)	1	11	0.33	0.33	0.00
	mg/L	2	19	3.19	3.21	-0.62
		3	19	1.49	1.42	4.93
	Cations	1	18	0.45	0.42	7.14
	(NH_4, Na, Ca,	2	24	3.93	3.96	1.81
	Mg, K)	3	18	1.10	1.02	7.84
	mg/L					

Table 3. Results Reported For All Analytes Except Heavy Metals--1088 Audit

Audit	Analyte	Sample	N	Average Reported Value	Expected Value	% Diff.
1088	pH	1	49	3.94	3.91	0.77
		2	49	4.25	4.27	-0.47
		3	48	3.71	3.68	0.82
	Conductivity	1	43	62.37	66.14	-5.70
	µS/cm	2	43	23.94	24.08	-0.58
		3	43	86.64	96.43	-10.15
	Acidity	1	11	116.00	124.00	-6.45
	µeq/L	2	11	64.78	53.67	20.70
		3	11	192.00	209.00	-8.13
	SO_4	1	34	2.55	2.11	20.85
	mg S/L	2	33	1.07	0.90	18.89
		3	35	4.80	4.01	19.70
	NO_3	1	35	1.04	0.87	19.54
	mg N/L	2	34	0.14	0.13	7.69
		3	34	0.14	0.11	27.27
	Anions (Cl, F)	1	16	1.29	1.27	1.58
	mg/L	2	13	0.38	0.32	18.75
		3	15	0.66	0.43	53.48
	Cations	1	27	2.46	2.38	3.36
	(NH_4, Na, Ca,	2	26	0.47	0.41	14.63
	Mg, K)	3	26	1.09	0.99	10.10
	mg/L					

Table 4. Table 3 Results After Outliers Removed

Audit	Analyte	Sample	N	Average Reported Value	Expected Value	% Diff.
1088	pH	1	49	3.94	3.91	0.77
		2	48	4.30	4.27	0.70
		3	48	3.71	3.68	0.82
	Conductivity	1	42	62.93	66.14	-4.85
	µS/cm	2	41	24.85	24.08	3.20
		3	39	93.53	96.43	-3.00
	Acidity	1	8	132.00	124.00	6.45
	µeq/L	2	6	53.43	53.67	-0.45
		3	8	235.00	209.00	12.44
	SO_4	1	29	2.12	2.11	0.47
	mg S/L	2	30	0.89	0.90	-1.11
		3	30	4.05	4.01	1.00
	NO_3	1	32	0.87	0.87	0.00
	mg N/L	2	29	0.12	0.13	-7.69
		3	31	0.11	0.11	0.00
	Anions (Cl, F)	1	13	1.32	1.27	3.44
	mg/L	2	8	0.32	0.32	0.00
		3	11	0.45	0.43	4.65
	Cations	1	27	2.46	2.38	3.36
	(NH_4, Na, Ca,	2	22	0.43	0.41	4.88
	Mg, K)	3	21	1.04	0.99	5.05
	mg/L					

Table 5. Concentrations of the Anions and Cations in Each 1988 Audit Sample[a]

	0588			1088		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Cl	0.280	2.738	1.254	1.078	0.283	0.349
F	0.051	0.474	0.167	0.191	0.039	0.084
NH_4	0.078	0.835	0.471	0.335	0.080	0.610
Na	0.186	1.771	0.393	1.340	0.179	0.235
Ca	0.047	0.388	0.038	0.115	0.047	0.046
Mg	0.021	0.063	0.042	0.068	0.028	0.017
K	0.084	0.798	0.078	0.524	0.073	0.077

[a]Expressed as mg analyte per L except for NH_4 which is mg N/L.

Table 6. Heavy Metal Results for Sample 4 of 0588 Audit

Laboratory	N[a]	Reported Value[b]	Expected Value	% Diff.
317003	7	0.97	0.96	1.04
320001	7	0.94	0.96	-2.08
334001	7	0.96	0.96	0.00
335002	7	0.92	0.96	-4.17
336001	7	0.97	0.96	1.04
339001	7	0.96	0.96	0.00
342002	7	1.02	0.96	6.25
345001	7	1.04	0.96	8.33
347003	7	0.92	0.96	-4.17
406001	4	0.78	0.82	4.88
412001	7	0.40	0.96	-58.33
436007	7	1.00	0.96	4.17
501001	7	1.01	0.96	4.99
506012	5	0.85	0.83	2.41
508016	7	0.99	0.96	3.13
517008	7	0.93	0.96	-3.13
525009	6	0.82	0.85	-3.53
529005	7	0.95	0.96	-1.04
542010	7	0.99	0.96	3.13
548005	5	0.80	0.83	-3.61

[a]N - the number of metals for which results were reported.

[b]The average concentration (mg per L) for all metals for which results were reported.

Table 7. Heavy Metal Results for Sample 5 of 0588 Audit

Laboratory	N[a]	Reported Value[b]	Expected Value	% Diff.
317003	7	0.33	0.33	0.00
320001	7	0.34	0.33	3.03
334001	7	0.33	0.33	0.00
335002	7	0.32	0.33	-3.03
336001	7	0.33	0.33	0.00
339001	7	0.34	0.33	3.03
342002	7	0.36	0.33	9.09
345001	7	0.40	0.33	21.21
347003	7	0.32	0.33	-3.03
406001	2	0.17	0.17	0.00
412001	7	0.32	0.33	-3.03
436007	7	0.39	0.33	18.18
501001	7	0.35	0.33	6.06
506012	5	0.26	0.26	0.00
508016	7	0.35	0.33	6.06
517008	7	0.32	0.33	-3.03
525009	6	0.26	0.27	-3.70
529005	7	0.33	0.33	0.00
542010	7	0.36	0.33	9.09
548005	5	0.26	0.26	0.00

[a]n = the number of metals for which results were reported.

[b]The average concentration (mg per L) for all metals for which results were reported.

Table 8. Heavy Metal Results for Sample 4 for 1088 Audit

Laboratory	N[a]	Reported Value[b]	Expected Value[b]	% Diff.
334001	7	0.85	0.79	7.59
335002	7	0.80	0.79	1.27
336001	6	0.81	0.76	6.58
342002	6	0.83	0.76	9.21
347003	7	0.82	0.79	3.80
353001	1	0.13	0.09	44.44
406001	6	0.79	0.71	11.27
412001	7	0.86	0.79	8.86
436007	7	0.85	0.79	7.59
501001	7	0.87	0.79	10.13
508016	7	0.84	0.79	6.33
521004	6	0.79	0.76	3.95
527002	7	0.91	0.79	15.19
529005	7	0.83	0.79	5.06
542010	6	0.77	0.76	1.32

[a]N = the number of metals for which results were reported.

[b]The average concentration (mg per L) for all metals for which results were reported.

Table 9. Heavy Metal Results for Sample 5 of 1088 Audit

Laboratory	N[a]	Reported Value[b]	Expected Value[b]	% Diff.
334001	7	0.43	0.41	4.88
335002	7	0.40	0.41	-2.44
336001	6	0.39	0.38	2.63
342002	5	0.40	0.38	5.26
347003	7	0.41	0.48	-14.58
353001	1	0.41	0.07	14.28
406001	6	0.40	0.40	0.00
412001	5	0.45	0.38	18.42
436007	7	0.43	0.41	4.88
501001	7	0.43	0.41	4.88
508016	7	0.40	0.41	-2.44
521004	5	0.38	0.38	0.00
527002	7	0.41	0.41	0.00
529005	6	0.42	0.40	5.00
542010	5	0.40	0.38	5.26

[a]N - the number of metals for which results were reported.

[b]The average concentration (mg per L) for all metals for which results were reported.

Table 10. Concentrations of the Heavy Metals in Each 1988 Audit Sample in mg Analyte/L

	0588		1088	
	Sample 4	Sample 5	Sample 4	Sample 5
Mn	0.034	0.019	0.030	0.019
Fe	0.082	0.049	0.081	0.007
Cd	0.034	0.019	0.030	0.018
Cu	0.070	0.029	0.056	0.041
Ni	0.022	0.014	0.022	0.018
Pb	0.110	0.054	0.089	0.067
Zn	0.610	0.142	0.482	0.238